

Development of nanocomposites based on polypyrrole and carbon nanotubes for supercapacitors

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ABSTRACT

Supercapacitors are recognized as one of the most promising energy storage devices for a wide range of civilian and military applications in electric vehicles, uninterruptible power supplies. Conducting polymer nanocomposites are new functional materials suitable for supercapacitors due to synergistic effect of individual components. In present work, polypyrrole/CNT nanocomposites have been prepared by an in-situ chemical polymerization method and studied for supercapacitor. CNTs were well functionalized using 3:1 ratio of H₂SO₄ and HNO₃ before polymerizing the pyrrole. Analytical techniques such as SEM, UV-VIS and FTIR were used to characterize the synthesized materials. The SEM images reveal that the materials have rough and granular morphology. The composites showed good interaction based on the shift to longer wavelengths in the electronic transition, indicating the interaction between PPy and functionalized CNTs as observed in their UV-VIS and FTIR spectra. The electrochemical performance was evaluated by using cyclic voltammetry (CV) in 1M Na₂SO₄ electrolyte and specific capacitance was obtained at 0.5 V/s for pure polypyrrole and PPy/CNT nanocomposites. Nanocomposite showed the enhanced electrochemical performance as compared to that of pure polypyrrole. The specific capacitance obtained at the scan rate 0.5V/s was found to be 0.825 F/cm² for pure polypyrrole and 1.0619 F/cm² for PPy/CNT nanocomposite material respectively, indicates that PPy/CNT nanocomposite is suitable material as electrode for supercapacitor as compared to pure polypyrrole. Copyright © 2014 VBRI press.

Keywords: Supercapacitor; polypyrrole; carbon nanotubes; cyclic voltammetry.



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Introduction

Due to the recent increase in energy demand worldwide, many laboratories are actively engaged in the development of materials which are flexible, lightweight and environmentally friendly and can be used as electrode material for supercapacitors also known as electrochemical capacitors. Supercapacitors are recognized as one of the most promising energy storage devices for a wide range of civilian and military applications in electric vehicles, uninterruptible power supplies as they have several advantages like long cycle life, short charge–discharge time and safety [1, 2]. Supercapacitors are designed to bridge the gap between batteries and capacitors to form fast charging energy-storage devices of intermediate specific energy. In general, the supercapacitors can be classified into electrical double-layer capacitors (EDLCs) and pseudo-capacitors. EDLCs employing carbonaceous materials as electrodes usually have high power density but suffer from low capacitance. While pseudo-capacitors using transition metal oxides and/or conductive polymers as electrode materials can provide high capacitance but suffer from poor cycling stability arising from their low conductivity. As a result, superior performance is expected from the combination of carbonaceous materials and conductive polymers [3, 4]. The major classes of materials applied for supercapacitors include various forms of carbon, transition metal oxides, and conductive polymers. Because the key factors determining the performance of supercapacitors are the specific surface area (SSA) of electrode materials, the properties of electrolytes, understanding and modifying the surface properties are crucial in achieving high power and energy density [5]. Various carbonaceous materials including activated carbon, CNTs and mesoporous carbon have been investigated as electrical double-layer capacitor (EDLC) electrodes [6, 7]. However, the carbon-based capacitors provide higher power density but much lower energy density than pseudocapacitors. Compared with conducting polymers in pseudocapacitors, the specific capacitance of carbon-based materials is relatively low. An alternative approach to improve energy density is to fabricate hybrid nanocomposite combining carbon nanotubes with conducting polymers [8]. Conducting polymers have large variety of applications [9, 10] which make this polymer suitable for gas sensor [11], functional hybrid [12], as pH switching electrical conducting biopolymer hybrid for sensor applications [13], as an electrically active redox biomaterial for sensor applications [14], as a matrix for preparation of conducting polymer nanocomposites [15]. Therefore, there has been increasing interest of the researchers for the preparation of nanocomposites based on conducting

polymers. The progress in the field of electrochemical supercapacitors employing conducting polymers during the past decade is reviewed, with special emphasis on electrochemical characterization techniques which resulted in better results showing good electrochemical behaviour. Recently there has been an extensive research carried on the electrochemical performance of composite of conducting polymers/carbon based materials [16-20] to improve the lacunas of individual materials. Many reports have also shown that the formation of polymer/CNT composites can be considered as a useful approach for the fabrication of polymer-based devices. The aim of this study is to fill the CNT in order to improve the interaction between the CNT and conducting polymer, which may lead to an increase in the electrical conductivity. Potential applications of these nanocomposites are in high energy portable electronics and supercapacitor properties [21]. Among all synthesized conducting polymers, polypyrrole (PPy) has potential uses in synthesizing polymer/CNT composites due to its environmental stability and excellent electrical conductivity. PPy can be prepared by chemical or electrochemical oxidation of pyrrole in various organic solvent and in aqueous media. Although electrochemical polymerization leads to formation of a conductive PPy thin film on the working electrode, it is not appropriate for the mass production. In contrast, chemical oxidative polymerization is simple, fast, cheap, and easily scaled up [22]. The polypyrrole can offer better inter-particle connectivity to the CNT in the composite could obviously offer high electronic conductivity and could also facilitate the easy access of the electrolyte into the bulk film by means of its mesopore [23].

Therefore, we report here the synthesis of pure conducting polypyrrole (PPy) and PPy/CNT nanocomposites by using an in-situ chemical oxidative method for the study of electrochemical performance to find the synergistic effect of both the components suitable for supercapacitors. The electrochemical performance of PPy/CNT nanocomposites is systematically compared with that of pure polypyrrole using cyclic voltammetry and determining specific capacitance along with their structural characterizations using SEM, FTIR and UV-VIS spectral analysis.

Experimental

Materials

The monomer pyrrole was purchased from Sigma-Aldrich (99%) and purified through distillation under reduced pressure and stored refrigerated before use. Multi-walled Carbon Nanotubes (MWCNTs) with purity 95% having an average diameter of 20 nm and length in few microns were obtained from NPL New Delhi, India

prepared using a conventional tube furnace by chemical vapour deposition (CVD) technique. All other reagents including FeCl_3 (purity 99.5%) as oxidant, H_2SO_4 (purity 78%), HNO_3 (purity 80%) for functionalization of MWCNTs were also purchased from Sigma–Aldrich and used as received without further purification. All chemicals used for the synthesis were of AR grade. All chemicals were of analytical grade. Solutions were prepared in de-ionized water.

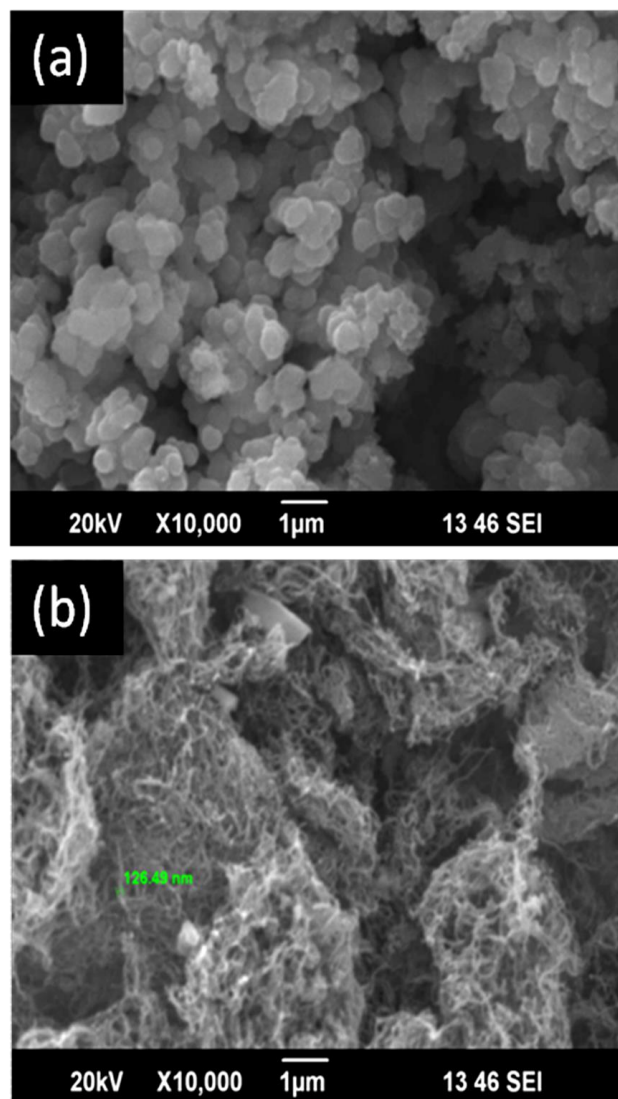


Fig. 1. SEM image of (a) pure PPy and (b) PPy/CNT.

Characterizations

The surface morphology of the synthesized nanocomposites was studied with the help of Scanning Electron Microscope (JEOL Model JSM - 6390LV). The formation of polymeric nanocomposites was confirmed by FTIR measured on Bruker Alpha model and absorbance spectra in UV-VIS range was measured on

Shimadzu UV-1800 spectrophotometer. Electrochemical studies were done using electrochemical analyser (CH Model 600D series). The pellets were prepared with the help of hydraulic press (Kimaya Engineers, India) by applying a pressure of 5000 kg/cm^2 .

Functionalization of MWCNTs

As-received MWCNTs were functionalized by chemically treated in the acid solution containing 6M H_2SO_4 and 6M HNO_3 in 3:1 ratio. MWCNTs were added to the acid solution and then sonicated for 4 hours at 50°C . After centrifugation MWCNTs were filtered, washed and dried to get functionalized MWCNTs [24].

Preparation of PPy/CNT nanocomposites

PPy/CNT nanocomposite was synthesized by an *in-situ* chemical oxidation polymerization. In a typical reaction, 100 mg of functionalized MWCNTs were first well stirred in 50 mL of an aqueous solution containing anhydrous ferric chloride (1.94 g FeCl_3). 500 μL of the pyrrole monomer was slowly added drop wise into this solution and the polymerization was allowed to continue for 4 h with constant stirring. The precipitated composite was filtered, washed thoroughly with de-ionized water, and then dried in a vacuum oven at 60°C for 12 h. The pure polypyrrole was also prepared by the same process but without adding MWCNT's for comparison [18].

Results and discussion

The SEM images of pure PPy and PPy/CNT nanocomposites are shown **Fig. 1(a)** and **1(b)** respectively. Morphologically PPy shows the existence of small globules and porous surface which can be beneficial for ion diffusion. PPy/CNT nanocomposite shows tubular and interwoven surface structure with an average diameter of 126 nm which indicates CNTs are well covered by polymer in the similar way as observed in the literature [25]. The FTIR spectra of pure PPy and PPy/CNT nanocomposite are shown in **Fig. 2(a)** and **2(b)** respectively. FTIR spectra of PPy showed the main characteristic peaks at 675 cm^{-1} corresponding to ring deformation, 929 cm^{-1} corresponding to C-H deformation, 1043 cm^{-1} C-H in-plane bend, 1188 cm^{-1} ring breathing, 1381 cm^{-1} and 1346 cm^{-1} corresponding to the fundamental vibrations of polypyrrole ring, The peak at 1585 cm^{-1} corresponding to C=C. The peak at 3348 cm^{-1} corresponds to the N-H bond. These peaks were observed in the present work for preparation of PPy using FeCl_3 as oxidant, this agreed well as per the literature, confirming the formation of polypyrrole. The FTIR spectra of PPy/CNT nanocomposite showed the other important bands observed at 2813 cm^{-1} and 2656 cm^{-1} which are due to the C-H stretching vibrations and strong peak at 761 cm^{-1} is due to the C-H bending, which

are the nanotube backbone vibrations thus confirming the formation of polypyrrole composite with CNT [18].

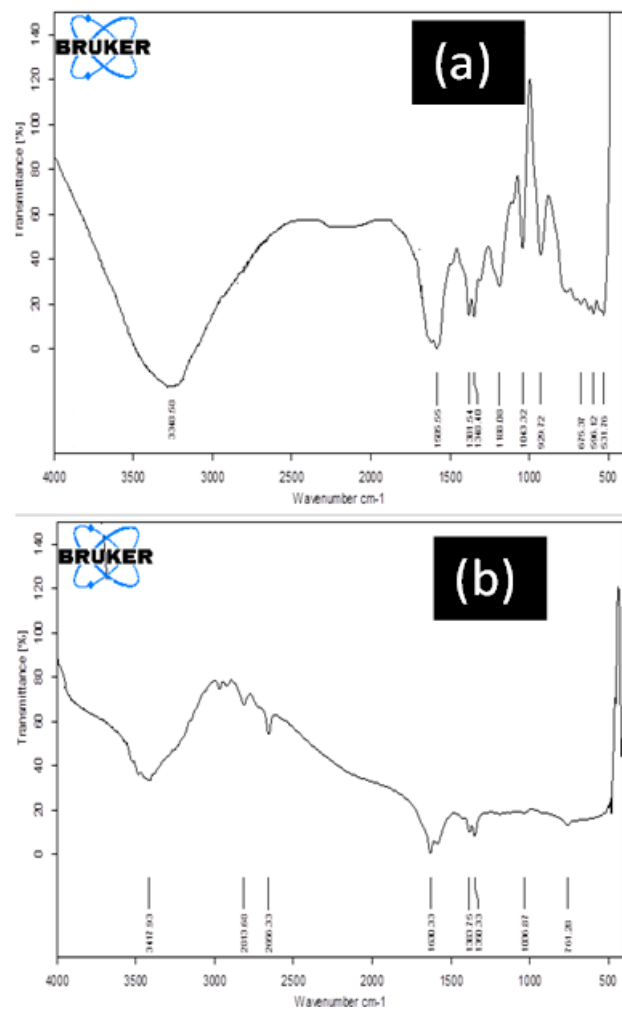


Fig. 2. FTIR spectra of (a) pure PPy and (b) PPy/CNT.

UV-Visible spectroscopy was performed to ascertain the interfacial interaction of PPy/CNT nanocomposites. The UV-Visible spectra of PPy and PPy/CNT are shown in Fig. 3. The pure polypyrrole shows two distinct bands at 294 nm and 420 nm. These two transitions corresponded to the transitions from valence bond to polarons and bipolarons of the oxidized form of polypyrrole. The characteristic band for the polaronic transition around 420 nm and the peak around 294 nm represents the π - π^* electron orbital transition along the backbone of the polymer chain. As CNTs were incorporated into polymer, the characteristic peaks assigned to the polaron- π^* transition and π - π^* transition of polymer chain shifted to shorter wavelengths,

indicating the interaction between polymer chain and CNTs.

The electrochemical characterization of materials is often carried out using galvanostatic charge-discharge, cyclic voltammetry and electrochemical impedance studies. These techniques are in fact not complimentary to each other in the context of design of supercapacitors; rather each one of them has individual merits. For example, in order to obtain reliable preliminary estimates of the specific capacitance, galvanostatic charge-discharge studies using a three electrode (working, reference and counter electrodes) assembly in a suitable medium are carried out. On the other hand, cyclic voltammetry provides information regarding the reversible nature of the electrode in a suitable electrolyte and the effect of the scan rate on the specific capacitance. The electrochemical impedance not only yields accurate estimates of specific capacitance but also gives insights into the synergistic effect of each interfacial parameter.

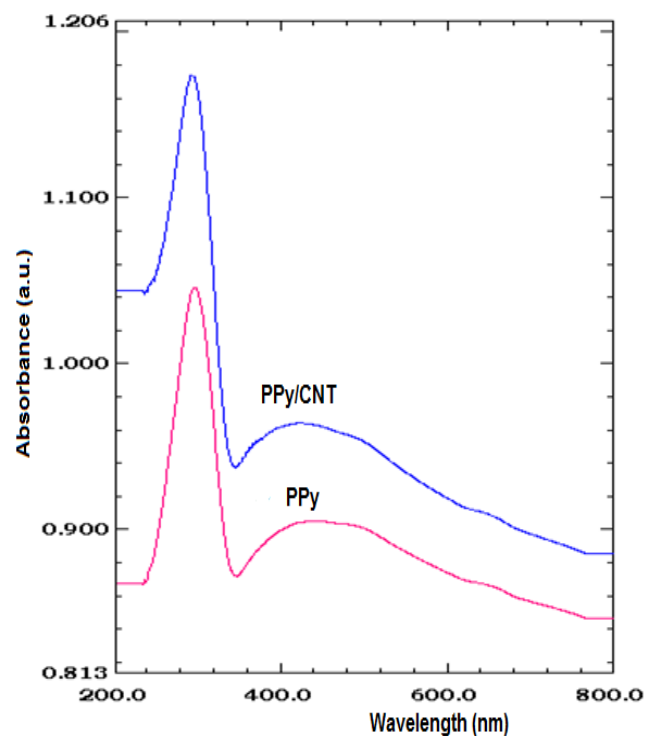


Fig. 3. UV-VIS spectra of (a) pure polypyrrole (PPY) (b) PPy/CNT.

Cyclic voltammetry is customarily employed for investigations of electron transfer processes in diverse contexts; however, in the analysis of supercapacitors, they are useful for (i) ascertaining the stability of the electrode; (ii) choosing the appropriate electrolyte and (iii) establishing the electrolyte concentrations [26]. It is well known that the potential window needs to be large

in the cyclic voltammetric experiment and hence organic electrolytes are more preferred since the aqueous electrolytes restrict the magnitude of the potential window to ~ 1 V. The specific capacitance (Fg^{-1}) from cyclic voltammetry is estimated [27] from the equation (1),

$$C = \frac{i}{vm} \quad \text{-----} \quad (1)$$

where, i denote the current, m is the mass loading and v represents the scan rate. If (m) is replaced by the area (A) of the electrode, capacitance per unit area is obtained in terms of Fcm^{-2} .

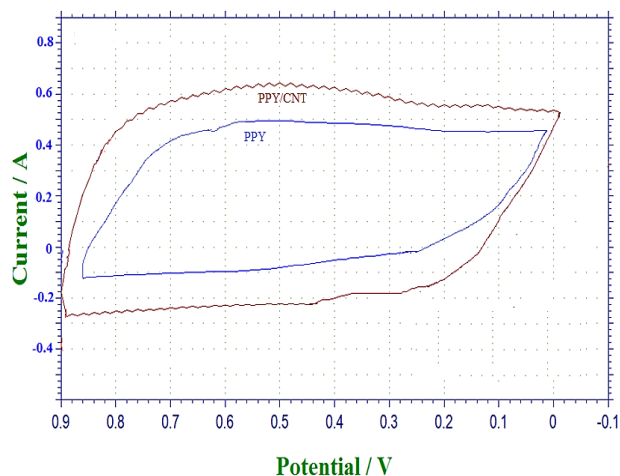


Fig. 4. CV of (a) PPY and (b) PPY/CNT in 1M Na_2SO_4 electrolyte solution in the voltage range of 0.1–0.9V at scan rate 0.5V/s.

The electrochemical performance of pure PPY and PPY/CNT nanocomposite electrodes was studied by cyclic voltammetric analysis in the three-electrode cell, the working electrode was the pellet of material, a platinum wire was the counter electrode, and Ag/AgCl was used as reference electrode. Electrochemical performance was depicted using cyclic voltammetry in which 1M Na_2SO_4 electrolyte solution was used in the voltage range of 0.1–0.9V at scan rate 0.5V/s as shown in **Fig. 4**. Even though the capacitance of conducting polymers are pseudocapacitive by nature, the ideal electric double layer capacitance (EDLC) behaviour of the cells has also been deduced from the parallelogram shapes of the CVs (i.e., the mirror images along the zero current line). The CVs of the cells show that the potential reversals at the potential limits are fast and instantaneous. This suggests that the adsorption/desorption process of the ions are very fast during cycling [28]. The specific capacitance obtained at 0.5V/s scan rate was found to be 0.825 F/cm^2 for pure polypyrrole and 1.0619 F/cm^2 for PPY/CNT nanocomposite material respectively, indicates that PPY/CNT nanocomposite is suitable material as electrode for supercapacitor as compared to pure PPY.

Conclusion

PPY/CNT nanocomposites and pure polypyrrole were synthesized successfully by using in-situ chemical oxidative polymerization. The formation of composite was confirmed by the FTIR and UV-VIS spectra. Morphologically pure polypyrrole shows granular and porous surface whereas the composite with CNT shows the tubular interwoven structure as observed from SEM images. The specific capacitance of PPY/CNT nanocomposite was found to be more than that of pure PPY indicating suitability of nanocomposites for supercapacitor.

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